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Direct C–N coupling of aniline to aminodiphenylamines with platinum-loaded titanium oxide photocatalyst

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Aminodiphenylamines (ADPAs) and their derivatives have been known to be used as dye intermediates and antioxidant of rubber. Due to its high demand in industrial production, the synthesis methods have been widely developed. In the present study, a photocatalytic synthesis route was examined, i.e., the photocatalytic C–N coupling of aniline in an alkaline solution with a Pt-loaded titanium oxide (Pt/TiO₂) photocatalyst. Nearly 20% of yield and 77% of selectivity were achieved with the Pt/TiO₂ photocatalyst for 30 min. It was found that this C–N bond formation showed a high dependence on the initial pH of solvent and irradiation light wavelength, i.e., the reaction can only proceed when pH > 11.79, and an incident light wavelength of 365 nm gave a high ADPAs selectivity. The mechanistic studies by using isotopic compounds suggested that the rate-determining step (RDS) for ADPAs production would be the formation of a transition complex with the rehybridization to sp³ on the aromatic ring of aniline. The UV-vis spectra analysis and Arrhenius plots further revealed the presence of three formation routes of ADPAs in the present system: The first one begins with the hole-oxidation of aniline by TiO₂ photocatalyst excited by UV light, the second one starts with one electron transfer from N atom in aniline to Ti in TiO₂, which only occurred with an incident light wavelength of 365 nm, and the last one is the oxidation of aniline molecules by hydroxyl radicals.

1. Introduction

The formation of carbon-nitrogen (C–N) bond is a fundamental process in organic chemistry, underpinning the synthesis of a wide array of compounds, including pharmaceuticals, agrochemicals, and natural products.^{1–3} Traditionally, C–N bond formation has been achieved through various classical methods such as nucleophilic substitution,^{4–6} reductive amination,^{7–10} the Buchwald-Hartwig^{11–13} and Ullmann coupling reactions.^{14–16} These methods have been proven effective, however, they often require harsh reaction conditions like high refluxing temperatures, bio-toxicity of aldehydes, organic halides. As the demand for more sustainable chemical processes continues to grow, there is a pressing need to develop green and mild synthetic methods for C–N bond formation.

Recent developments of photocatalysis have opened new avenues for C–N bond formation,¹⁷ offering a more environmentally friendly and versatile alternative to traditional methods. Titanium oxide (TiO₂), as the most common heterogeneous photocatalyst, due to its high chemical stability and low cost, has been developed successfully to construct C–N bond for a few synthetic applications, for example, N-alkylation^{18–20} and N-heterocycle formation.^{21,22} Our group also reported direct aromatic ring amination^{23,24} and alkenes hydroamination²⁵ by ammonia aqueous with metal loaded TiO₂ photocatalysts.

On the other hand, aniline has been applied for manufacturing of dyes, rubber, polymers, pharmaceuticals, and so on.^{26,27} Many attempts have been made to photocatalytically convert it into some value-added products, such as azobenzene, azoxybenzene, and nitrosobenzene.^{28–30} In this study, we examined the direct C–N coupling of aniline to produce 2-aminodiphenylamines (ADPA) and 4-amindipheylamines (4-ADPA), which have highly demand for dye intermediates and rubber antioxidants, with platinum-loaded TiO₂ photocatalyst (Pt/TiO₂) under UV light illumination. A series of experiments revealed the high pH dependence and wavelength dependence of these ADPAs formation. Kinetic experiments with isotopic compounds, and temperature-controlled reactions elucidated the formation mechanism in the present conditions.

2. Experimental

2.1 Materials

Commercial TiO₂ samples (Ishihara Sangyo Kaisha, ST-01, anatase, 300 m² g^{−1}), aqueous metal precursor solutions like H₂PtCl₆ (Nacalai Tesque, 99%), H₂AuCl₄ (Nacalai Tesque, 99%), PdCl₂ (Kishida Chemical, 99%), and AgNO₃ (Kishida Chemical, 99%) were applied for catalysts preparation. All of reagents employed in the photocatalytic reaction tests were commercially purchased and used without further purification: sodium hydroxide solution (NaOH (aq), Nacalai Tesque, 1 mol L^{−1} and 0.1 mol L^{−1}), hydrochloric acid solution (HCl (aq), Nacalai Tesque, 0.1 mol L^{−1}), acetonitrile (Nacalai Tesque, 99.5%), 1-octanol (Kishida Chemicals, 99.5%), aniline (Nacalai Tesque, 99%), aniline-*d*₅ (Cambridge Isotope Laboratories, ≥98%), aniline-*d*₇ (Cambridge Isotope Laboratories, ≥98%), azobenzene

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(Sigma-Aldrich, 96%), hydrazobenzene (Tokyo Chemical Industry, >98%), 2-aminodiphenylamine (Tokyo Chemical Industry, >98%), 4-aminodiphenylamine (Tokyo Chemical Industry, >98%).

2.2 Preparation of catalysts

A typical photodeposition method was used to synthesize various metal(M)-loaded titanium oxide photocatalysts, $M(x)/TiO_2$, where x shows a loading amount of the metal cocatalyst as weight percent (wt%) of the photocatalyst. The preparation procedure of representative $Pt(1.0)/TiO_2$ photocatalyst is described as follows. 1.0 g of TiO_2 powder was dispersed in 200 mL of ion-exchanged water and was irradiated with a xenon lamp (PE300BUV, 300 W) for 30 min with magnetically stirring to clean the TiO_2 surface. Then, 50 mL of methanol and 530 μ L of prepared H_2PtCl_6 solution (18.84 g L^{-1} as Pt) were added to the suspension as a hole scavenger and a metal precursor, respectively. The contents were stirred for 15 min without irradiation, followed by stirring for 1 h under light irradiation. The resulted suspension was filtered with suction and was washed with 500 mL of ion-changed water 3 times. After drying over 12 h under 353 K in an electronic oven, a grey-colored powder of the $Pt(1.0)/TiO_2$ sample was obtained. The XRD pattern (Fig. S1) of the prepared $Pt(1.0)/TiO_2$ sample suggested the anatase phase of TiO_2 remains after Pt loading, and no characteristic peaks of Pt were observed, which may attribute from a small loading amount and the small size of Pt nanoparticles. According to TEM images revealed that the average diameter of highly dispersed Pt nanoparticles was 2.06 nm (Fig. S2). Due to the Pt loading, comparing to the bare TiO_2 sample, this $Pt(1.0)/TiO_2$ sample showed a strong visible light absorption in the DR UV-vis spectrum. (Fig. S3). Other $M(x)/TiO_2$ samples were prepared by the same procedure mentioned above with the different amount of desired metal precursor.

2.3 Photocatalytic reaction tests

The photocatalytic reaction test was carried out in a sealed test tube (20 mL) as a closed reactor. A typical experiment procedure was as follows. As a pretreatment, light irradiation from a xenon lamp (PE300BUV, 300 W) was conducted without any optical filter for 30 min to clean up the surface of 50 mg of the $Pt(1.0)/TiO_2$ photocatalyst. Then, 4 mL of 0.1 mol L^{-1} NaOH (aq, the actual pH was measured as 12.70) and 4.6 μ L (50 μ mol) of aniline were added as a solvent and the only reactant, respectively. The amount reactant was measured by electronic balance before each reaction. And the test tube was plugged by a silicone septum stopper and sealed. By using an argon gas bubbling flow (30 mL min^{-1}) for 20 min, the existed air was purged. The contents were stirred with a UV-LED light irradiation (LC-L1V3 spotlight source) for the desired time (typically, 30 min) to promote the photocatalytic reaction. During the reaction, the reaction temperature was controlled at 298 K by a water bath with a cooling system. After the reaction, the suspension was firstly diluted by acetonitrile (CH_3CN) and filtered by using a syringe equipped with a PTFE membrane filter. The obtained liquid phase was then analyzed qualitatively

and quantitatively by GC-MS (Shimadzu QP-2020) and GC-FID (Shimadzu GC-2014) using 1-octanol as an internal standard. In some of reaction tests, 0.5 mL of the gaseous phase was extracted and analyzed by GC-TCD (Shimadzu GC-8A) to detect the production of H_2 gas after reactions.

2.4 Mechanistic studies

To investigate the formation mechanism of detectable products, a few kinetic experiments were carried out by using isotope labelled compounds, aniline- d_5 ($C_6D_5NH_2$) and aniline- d_7 ($C_6D_5ND_2$). And the apparent activation energies of each detectable products were calculated from a series of temperature-controlled experiments. The reaction temperature was controlled in a range of 296–306 K by using the water bath as mentioned.

2.5 Characterization

X-ray diffraction (XRD) patterns of samples were measured at room temperature using a Shimadzu Lab X XRD-6000 with Cu K α radiation (40 kV, 30 mA). The transmission electron microscopy (TEM) images were taken by a JEM-2200FS. The diffuse reflectance (DR) UV-vis spectra of the powder samples were recorded by using a JASCO V-770 spectrophotometer equipped with an integrating sphere, where $BaSO_4$ was used as a reference. The same spectrophotometer was also applied to measure the UV-vis spectra of liquid sample in a transmittance mode.

3. Results and discussion

3.1 Outline of the photocatalytic reaction tests

Table 1 shows the results of photocatalytic reaction tests. When the $Pt(1.0)/TiO_2$ sample was used in the present conditions (See the footnote), 2-aminodiphenylamine (2-ADPA, 8.99% yield) and 4-aminodiphenylamine (4-ADPA, 10.5% yield) were observed as main products (entry 1). Our previous study has reported another simple C–N bond coupling reaction,³¹ i.e., the photocatalytic amination of benzene by ammonia (NH_3) to form aniline, where the N–H bond in an ammonia can be activated by photogenerated holes (h^+) on Pt/TiO_2 photocatalyst to form an amide radical ($\bullet NH_2$) and it attacks aromatic ring to form C–N bond. This mechanism would be possibly applicable in present study. The control experiment results listed in Table S1 revealed that this C–N bond formation from aniline did not occur without photoirradiation or without photocatalyst, indicated that the formation of ADPAs (2-ADPA and 4-ADPA) was photocatalytically promoted. Another isomer of ADPA, i.e., 3-aminodiphenylamine (3-ADPA), was not found in the resulting mixture, which may attribute to the electron donating property of amino group ($-NH_2$) in aniline. After the formation of ADPAs, the successive reaction can occur since the amino group in ADPAs can activated again and yield some oligomers or polyanilines when the reaction time was extended, and thus led to a decrease of ADPAs selectivity (from 77.0% at 30 min to 37.3% at 720 min, Fig. S4). The UV-vis spectra of the solutions after the reaction showing a broad the absorption peak from

500 nm to 600 nm (**Fig. S5**) confirmed the formation of byproduct was azobenzene (AZB), a N=N bond coupling product oligomers or polyanilines.^{32,33} Another observed organic resulting from the activation of amino group,

Table 1 Photocatalytic conversion of aniline in various conditions ^a

Aniline $\xrightarrow[\text{NaOH(aq)}]{h\nu, \text{Pt(1.0)/TiO}_2}$ 2-Aminodipheylamine 4-Aminodipheylamine Azobenzene 2-ADPA 4-ADPA AZB								
Entry	Photocatalyst	Solvent (solvent pH) ^b	C (%) ^c	Y (%) ^d			S (%) ^e	H ₂ (μmol)
				2-ADPA	4-ADPA	AZB		
1	Pt(1.0)/TiO ₂	NaOH (aq) ^f (pH=12.70)	25.3	8.99	10.5	4.16	77.0	6.09
2 ^g	Pt(1.0)/TiO ₂	NaOH (aq) (pH=12.70)	/	/	/	/	/	6.46
3	Pt(1.0)/TiO ₂	CH ₃ CN	1.63	tr. ^h	tr.	0.353	0	2.22
4	Pt(1.0)/TiO ₂	HCl (aq) ⁱ (pH=3.29)	0	n.d. ^j	n.d.	n.d.	/	0.844
5	Pt(1.0)/TiO ₂	H ₂ O ^k (pH=6.58)	0	n.d.	n.d.	n.d.	/	0.916
6	Pt(1.0)/TiO ₂	NaOH (aq) ^l (pH=11.79)	1.82	n.d.	n.d.	n.d.	/	2.13
7	TiO ₂	NaOH (aq) (pH=12.70)	0	n.d.	n.d.	n.d.	/	0.0461
8	Ag(1.0)/TiO ₂	NaOH (aq) (pH=12.70)	3.21	1.00	0.927	0	60.1	0.0670
9	Pd(1.0)/TiO ₂	NaOH (aq) (pH=12.70)	4.58	1.19	1.01	0	48.1	1.10
10	Au(1.0)/TiO ₂	NaOH (aq) (pH=12.70)	2.52	0.934	0.679	0.851	64.1	1.63

^a Reaction conditions: 50 mg of photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of different solvents were applied; Reaction time: 30 min; The wavelength of the incident UV-LED light was at 365 ± 5 nm in wavelength, the irradiated light intensity was 1035 mW cm⁻² when measured at 360 ± 20 nm in wavelength; ^b The actual solvent pH was measured by a pH meter; ^c Conversion of aniline, C (%) = 100 × (introduced aniline – aniline remnant after the reaction)/(introduced aniline); ^d Yield of detectable products, Y (%) = 100 × A_(2-ADPA, 4-ADPA, AZB) × 2/(introduced aniline), where A_(2-ADPA, 4-ADPA, AZB) stands for the yielded amount of 2-ADPA, 4-ADPA, and AZB, respectively. ^e Selectivity of formed 2-ADPA and 4-ADPA based on consumed aniline, S (%) = 100 × (A_(2-ADPA) + A_(4-ADPA)) × 2/(introduced aniline – aniline remnant); ^f The commercial-purchased 0.1 mol L⁻¹ of NaOH (aq) was applied; ^g The reaction was proceeded without adding aniline as reactant; ^h tr. = not detected in GC-FID, but appeared characteristic mass peak in GC-MS; ⁱ The applied HCl (aq) was diluted from 0.1 mol L⁻¹ of HCl (aq); ^j n.d. = not detected in GC-MS and GC-FID; ^k Ion-changed water was applied; ^l The applied NaOH (aq) was diluted from 0.1 mol L⁻¹ of NaOH (aq).

which was already reported in some studies about the photocatalytic oxidation of aniline.^{30,34–36} In those reported studies, other byproducts were confirmed, such as benzoquinone, nitrosobenzene, and aminophenol, while they were not found in the present study, probably due to the absence of O₂ molecular and a relatively high concentration of aniline in NaOH aqueous solutions (12.5 mmol L⁻¹), where the radical reactions have great chance of occurring between aniline-related species. A series of optimization experiments in

different initial concentrations of aniline were conducted. The results were listed in **Table S2** and plotted in **Fig. S6**, from which the 12.5 mmol L⁻¹ of aniline showed best yield and selectivity of ADPAs and was applied as the standard concentration in this study. In the present reaction conditions, only H₂ (6.09 μmol) was detected as a gaseous product, no O₂ that might be possibly formed in water splitting was found. The calculated H₂ evolution (7.16 μmol) from the obtained ADPAs (5.02 μmol) and AZB (1.07 μmol) was close to the detected one, which hinted that such H₂

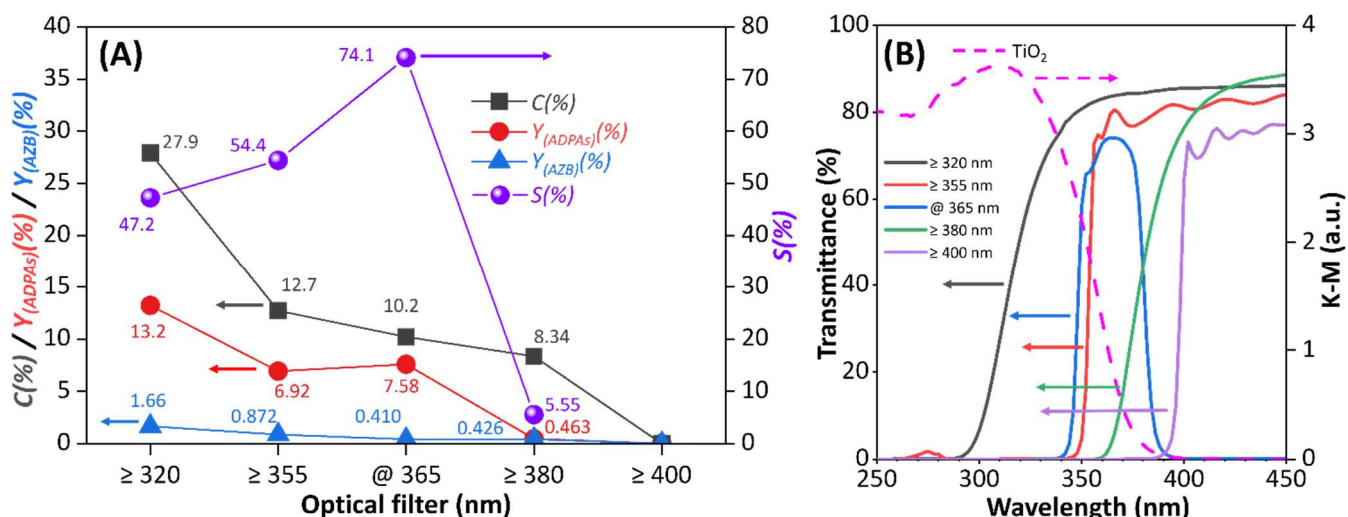
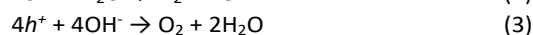
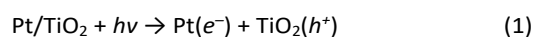


Fig. 1 (A) Results of photocatalytic tests for aniline conversion by using various optical filters. (B) Left y-axis: The transmission spectrum of each optical filter used in the photocatalytic test, where each permitted wavelength of long pass filters was longer than 320, 355, 380, and 400 nm, respectively and that of the band-pass filter was around 365 nm; Right y-axis: DR UV-vis spectra of the TiO₂ sample (broken line). Reaction conditions: 50 mg of the Pt(1.0)/TiO₂ photocatalyst; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of NaOH (aq, pH = 12.70) was applied as solvent; The xenon lamp was applied as light source with different filters; The original irradiated light intensity was 50 mW cm⁻² when measured at 360 ± 20 nm in wavelength; Reaction time: 30 min. C (%) = 100 × (introduced aniline – remained aniline after the reaction)/(introduced aniline); Y_(ADPAs) (%) = 100 × (A_(2-ADPA) + A_(4-ADPA)) × 2/(introduced aniline), Y_(AZB) (%) = 100 × A_(AZB) × 2/(introduced aniline), where A_(2-ADPA, 4-ADPA, AZB) stands for the yielded amount of 2-ADPA, 4-ADPA, and AZB respectively; S (%) = 100 × (A_(2-ADPA) + A_(4-ADPA)) × 2/(introduced aniline – remained aniline).

production was possibly from a dehydrogenative C–N and N=N coupling of aniline. However, in **entry 2**, without adding any aniline as reactant, almost same i.e., 6.42 μmol of H₂ and zero of O₂, which suggested that such H₂ evolution was probably from the decomposition of alkaline water as reported in the absence of aniline (eqs. 1 and 2).^{37–40} Since aniline is more easily oxidized by photogenerated holes in TiO₂ photocatalyst than water (eq. 3), aniline can be oxidized instead of water, i.e., the presence of aniline would inhibit the water oxidation and produce ADPAs and AZB without observation of O₂ gas evolution. In both cases (**entry 1** and **entry 2**), the exact pH of reaction suspensions remained almost no change after the photocatalytic tests (12.69 and 12.70 respectively), suggesting that the consumption of OH⁻ by the photogenerated holes (eq. 3) was very limited. The slightly decreased pH value in **entry 1** (from 12.70 to 12.69) possibly resulted from the measurement error of pH meter, since the OH⁻ either abstracts H⁺ in aniline radical cation to give H₂O or is oxidized into OH• and react with aniline to produce H₂O (The details will be provided later), then the formed H₂O is reduced by electrons to give H₂ and release OH⁻ (eq. 2) again to keep a constant pH value.

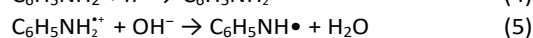
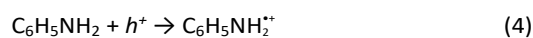


To elucidate the solvent effect, some reaction tests were conducted with other solvents, such as acetonitrile (CH₃CN), H₂O and HCl (aq). In CH₃CN (**entry 3**), only trace amount of ADPAs and 0.353 μmol of AZB were obtained, which suggested

that the photogenerated holes (h⁺) can hardly activate the aniline molecules to form C–N bond and N–N bond in present conditions. And the observed small amount of H₂ production (2.22 μmol) was due to photocatalytic dehydrogenative formation of succinonitrile (NCCH₂–CH₂CN) and 4-aminobenzeneacetonitrile (NCCH₂–C₆H₅NH₂) from the homo-coupling of CH₃CN and the cross-coupling of aniline and CH₃CN,^{41–43} as they were qualitative distinguished by GC-MS in a trace amount.

When the initial pH of the aqueous solvent was 3.29, 6.58, and 11.79 respectively (**entries 4–6**), no detectable organic products. Slightly increased amount of H₂ production was confirm when pH was 11.79. Considering the pK_a of aniline is 4.63,⁴⁴ in the acidic condition (**entry 4**, pH = 3.29), most of aniline molecules were existed in a cation form (C₆H₅NH₃⁺), which were unfavourable to be adsorbed on the positively charged TiO₂ surface due to the electric charge repulsion (the isoelectric point of TiO₂ is around 6) and the difficulty of the N–H bond activation in the positively charged amino group by holes. While the results in **entries 5** and **6** hinted that without the enough concentration of OH⁻ in the solution, even the aniline molecules were in usual form (C₆H₅NH₂), the photocatalytic conversion can hardly proceed. Furthermore, the reaction tests under various aqueous solutions with different initial pH confirmed that the ADPAs and AZB can be obtained only when the pH > 11.79 (**Table S3, entries 7–11**). The requirement on high concentrated OH⁻ solution may be related with the following possible processes, i.e., (i) Abstraction of the hydrogen atom by OH⁻ from the aniline radical cation species to generate anilino radical species (C₆H₅NH₂•, pK_a of 7)⁴⁵ (eqs. 4 and

5); (ii) The photooxidation of OH^- by holes to produce hydroxyl radical species ($\text{OH}^\bullet$) (eq. 6), and the formed $\text{OH}^\bullet$ can attack aniline molecules to give the same anilino radical species (eq. 7). In a study about photocatalytic oxidation of aniline to AZB in the presence of O_2 , the author observed the same pH dependence on the AZB formation ($8.3 < \text{pH} < 12.3$) in a low aniline concentration basic solution ($0.0215 \text{ mmol L}^{-1}$) and confirmed that the holes were the primary oxidants to active aniline molecules rather than hydroxyl radicals,³⁰ which also supports the present case with the higher aniline concentration (12.5 mmol L^{-1}). Thus, the first case would be more likely; the hydrogen abstraction requires high pH conditions (eq. 5). The optimistic pH with the highest selectivity to ADPAs (77.0 %) was found at 12.70 and decreased to 39.3 % at 13.43 (Table S2, entries 9–11) because of an obvious photocatalyst aggregation with the increasing of pH as observation.



Various photocatalysts were examined in the best conditions for the photocatalytic reactions (Table 1, entries 7–10). For the bare TiO_2 sample (entry 7), there was no detectable organic products but $0.0461 \mu\text{mol}$ of H_2 , suggesting that both the formation of the coupling products and the photocatalytic H_2 production require cocatalyst that contribute to efficient charge separation. The $\text{Ag}(1.0)/\text{TiO}_2$, $\text{Pd}(1.0)/\text{TiO}_2$, and $\text{Au}(1.0)/\text{TiO}_2$ photocatalyst samples exhibited relatively low activities (entries 8–10), which indicated that Pt would be the most effective loaded metal cocatalyst for the coupling products and hydrogen formation. It was also consistent to our previous report that Pt/TiO_2 photocatalyst well promotes the ammonia decomposition through N–H bond activation to nitrogen and hydrogen.⁴⁶ The highest H_2 evolution with the $\text{Pt}(1.0)/\text{TiO}_2$ sample also consists with our previous study that Pt nanoparticles can play a catalytic role for the coupling of hydrogen radical species to yield H_2 molecules.⁴⁷

3.2 Wavelength dependency for products formation

As shown in Fig. 1A, the formation of ADPAs showed a strong dependence toward the incident light wavelength. Fig. 1B shows the property of the optical filters and the absorption band of TiO_2 . When the reaction was conducted with visible light irradiation ($>400 \text{ nm}$), no detectable product was found, as no corresponding light absorption for TiO_2 photocatalyst (Fig. 1B, S3). When UV light was irradiated, the total yield of detectable products increased with the increase of the light absorption of TiO_2 that realized by extending permitting wavelength. It is notable that the product selectivity was also varied with the light conditions and the best selectivity to ADPAs, $S(\%) = 74.1$ was achieved when the bandpass filter permitting around 365 nm light was applied. Such kind of high selectivity may be related to two reasons as follows. One is the avoidance

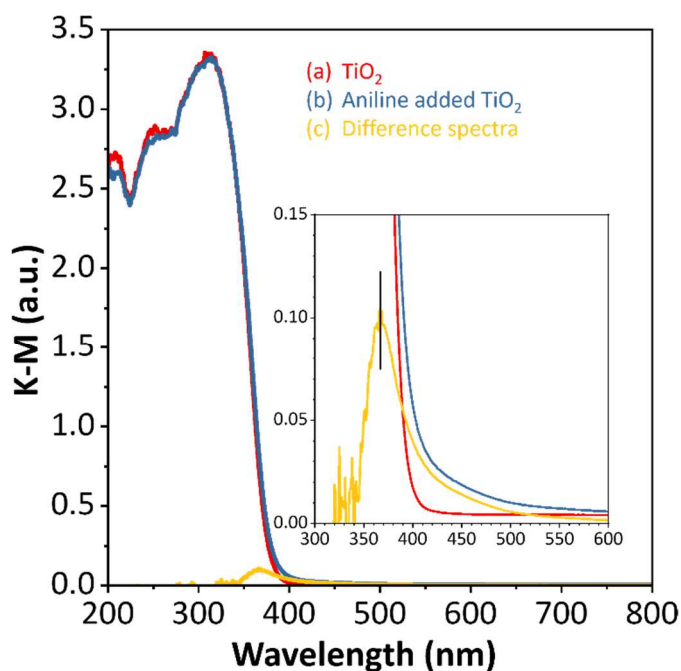


Fig. 2 DR UV-vis spectra of (a) TiO_2 powder, (b) aniline adsorbed TiO_2 powder ($200 \mu\text{mol}$ of aniline mixed with 200 mg of TiO_2 powder), and (c) their difference spectra. The inset shows enlarged plot from 300 nm to 600 nm .

of potential photolysis of aniline and ADPAs. As their UV-vis spectra shown in Fig. S7, no absorption was found for aniline and ADPAs in the region of longer than 350 nm in wavelength. The other is a specific photoexcitation of aniline adsorbed on the TiO_2 surface. The Fig. 2 revealed that when a small amount of aniline mixed with the TiO_2 powder, an adsorption edge shift was observed in the DR UV-vis spectrum (Fig. 2 a and b). The difference spectrum between them clearly suggested that a specific absorption band appeared around at 365 nm due to the interaction between aniline and TiO_2 surface (Fig. 2c). This band is different from the absorption bands of aniline or products in their UV-vis spectra (Fig. S6), suggesting that a surface complex consisting of aniline and TiO_2 surface would be formed and photoexcited by the light of 365 nm in wavelength.

Similar interaction between adsorbates and TiO_2 has already been reported, like benzyl amine,⁴⁸ pyridine,⁴⁹ and ammonia⁵⁰ on TiO_2 surface. In those studies, the photocatalytic reaction can be selectively mediated in visible light irradiation via photoexcitation at the N–Ti coordinate bond, where electron of N atom is excited by a charge transfer to Ti belonging to the conduction band of TiO_2 . Thus, for the present photocatalytic conversion of aniline to ADPAs, it is necessary to consider two formation routes, the one proceeds by the light in the range of $320\text{--}400 \text{ nm}$ in wavelength with the photoexcitation of TiO_2 photocatalyst, and the other is the selective reaction promoted by the light of around 365 nm in wavelength starting from the photoexcitation at the N–Ti coordinate bond. This will be discussed in detail later. It is also noticed that there was a broad absorption edge from 400 nm to 500 nm (Fig. 2, inset), which

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Table 2 Results of photocatalytic reaction tests with isotopic compounds. ^a

(1)

Aniline-*h7* 2-ADPA-*h* 4-ADPA-*h* AZB-*h*

(2)

Aniline-*d5* 2-ADPA-*d9* 4-ADPA-*d9* AZB-*d*

(3)

Aniline-*d7* 2-ADPA-*d12* 4-ADPA-*d12* AZB-*d'*

$Y(\%)^b$

Entry	Substance	2-ADPA ^c	4-ADPA ^d	AZB ^e	<i>ortho/para</i> ^f	k_H/k_D (ADPAs)	k_H/k_D (AZB)
1	aniline- <i>h</i>	9.24±0.25	10.6±0.15	4.49±0.30	0.872	-	-
2	aniline- <i>d5</i>	9.58±0.22	9.59±0.23	3.96±0.064	0.999	1.03 ^g	1.13 ⁱ
3	aniline- <i>d7</i>	9.09±0.49	8.97±0.22	2.16±0.66	1.01	1.06 ^h	1.83 ^j

^a Reaction conditions: 50 mg of Pt(1.0)/TiO₂ photocatalyst was used; 4.6 μL (50 μmol) of aniline-*h* (**entry 1**), aniline-*d5* (**entry 2**), and aniline-*d7* (**entry 3**) were introduced as the reactants respectively; 4 mL of NaOH (*aq*, pH = 12.70) was added as solvent; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm⁻² when measured at 360 ± 20 nm in wavelength; Reaction time: 30 min; For aniline-*d5* (**entry 2**) and aniline-*d7* (**entry 3**), the corresponding deuterated products were confirmed by GC-MS;

^b Yield of products was presented with standard deviation, $Y(\%) = 100 \times A_{(2-ADPA, 4-ADPA, AZB)} \times 2 / (\text{introduced aniline})$, where $A_{(2-ADPA, 4-ADPA, AZB)}$ stands for the yielded amount of usual or deuterated 2-ADPA, 4-ADPA, and AZB respectively; ^c yield of usual 2-ADPA (2-ADPA-*h*, **entry 1**) and deuterated 2-ADPA (2-ADPA-*d9* in **entry 2** and 2-ADPA-*d12* in **entry 3**); ^d yield of usual 4-ADPA (4-ADPA-*h*, **entry 1**) and deuterated 4-ADPA (4-ADPA-*d9* in **entry 2** and 4-ADPA-*d12* in **entry 3**); ^e yield of usual AZB (AZB-*h*, **entry 1**) and deuterated AZB (AZB-*d* in **entry 2** and AZB-*d'* in **entry 3**); ^f The ratio of produced 2-ADPA to 4-ADPA, $ortho/para = Y_{(2-ADPA)} / Y_{(4-ADPA)}$; ^g $k_H/k_D = (Y_{(2-ADPA-h)} + Y_{(4-ADPA-h)}) / (Y_{(2-ADPA-d9)} + Y_{(4-ADPA-d9)})$; ^h $k_H/k_D = (Y_{(2-ADPA-d9)} + Y_{(4-ADPA-d9)}) / (Y_{(2-ADPA-d12)} + Y_{(4-ADPA-d12)})$; ⁱ $k_H/k_D = Y_{(AZB-h)} / Y_{(AZB-d)}$; ^j $k_H/k_D = Y_{(AZB-d')} / Y_{(AZB-d')}$.

probably arise from a formation of a ligand-to-metal charge-transfer (LMCT) complex of aromatic ring adsorbed on TiO₂ surface with a [Ti⁴⁺...π] interaction,^{51,52} which gave a light brownish color of the TiO₂ sample adsorbing aniline.

3.3 Kinetic experiments

To get insight into the formation mechanism of 2-ADPA and 4-ADPA, three parallel reactions were conducted by applying usual aniline (aniline-*h7*) and deuterated anilines (aniline-*d5*

and aniline-*d7*) as reactants (**Table 2**). When aniline-*d5* was the reactant, no kinetic isotope effect (KIE) was observed on the ADPAs ($k_H/k_D = 1.03$, **entry 2**). This result indicated that cleavage of C–H bond in aromatic ring of aniline was not the rate-determining step (RDS) for the formation of 2-ADPA or 4-ADPA. However, the ratio of 2-ADPA production to 4-ADPA production in the case of aniline-*d5* changed from 0.872 (**entry 1**) to 0.999 (**entry 2**), even the total yield of ADPAs remained no change, suggesting that when aniline-*d5* was as the reactant, the *ortho* product (2-ADPA) was more favorably produced than *para*

product (4-ADPA). It could be explained by the bond length difference between the C–H of the usual aniline and the C–D of aniline-*d*5. In the deuterated molecule, the C–D bond is shorter than the C–H bond, which provides a lower steric effect when another aniline-*d*5 molecule approaches the *ortho* site to form a sp³-type transition complex as mentioned later. Also, no KIE was observed for ADPAs production when aniline-*d*7 molecule was used ($k_H/k_D = 1.06$, **entry 3**), suggesting that the N–H bond cleavage was not the RDS for ADPAs formation. Considering the bond dissociation energy (BDE) of C₆H₅NH–H (386 kJ mol^{−1}) is weaker than that of H–C₆H₄NH₂ (472 kJ mol^{−1} as H–C₆H₅ in benzene),⁵³ if both two bonds in aniline were able to be activated to form corresponding radical species, the RDS should be the most difficult step, i.e., the C–H bond fission of aromatic ring in aniline molecule. However, the presented k_H/k_D value shown in **entries 2** and **3** were almost unity. This pointed out another possibility, i.e., the formed anilino radical attacks another aniline molecule to give a transition complex with rehybridization (eq. 8), such as sp² to sp³ in a radical addition-elimination mechanism like in our previous study.^{31,54,55}



On the other hand, a secondary KIE was found for the production of AZB for aniline-*d*5 reactant ($k_H/k_D = 1.13$, **entry 2**). Considering that the formation of AZB is only related to the N–H bond breaking in aniline, such value over-unity but close to the unity would be due to stabilization effect of D atoms on the aromatic ring. A clear KIE was shown in **entry 3** on AZB production ($k_H/k_D = 1.83$) hinted that dissociation of one of several N–H bonds was the RDS in the process of AZB formation.

3.4 Temperature controlled experiments

To investigate the apparent thermal activation energy (E_a) of various products in this photocatalytic reaction, temperature-controlled photocatalytic reactions were conducted at 296–306 K. The pseudo-Arrhenius plots for products formation rate gave the apparent thermal activation energies for the productions of 2-ADPA, 4-ADPA, and AZB to be 15.9 kJ mol^{−1}, 7.57 kJ mol^{−1}, and 72.7 kJ mol^{−1}, respectively (**Fig. 3**). The quite low E_a value for ADPAs formation suggests that such kind of C–N bond formation process would be a purely photocatalytic process like our previous researches for photocatalytic C–C bond formation and C–N bond formation^{25,56} with Pt(1.0)/TiO₂ photocatalyst.

Meanwhile, for the formation of AZB, a relatively high E_a value indicates that besides the photoenergy, the thermal energy also assisted at least one step, which is the thermally RDS step. According to the kinetic experiments, probably one of the N–H bond dissociation processes for the AZB production was promoted by the thermal energy. In literatures^{30,34–36}, it has been well-known that in the photocatalytic oxidation reaction of aniline, AZB was a main product formed through a hydrogen abstraction process of hydrazobenzene (HyAZB) by O₂ (if existed), h^+ (eq. 9) and OH• (eq. 10). Considering that the anilino radicals were the predominant active aniline-related species in present conditions, the HyAZB should be mainly

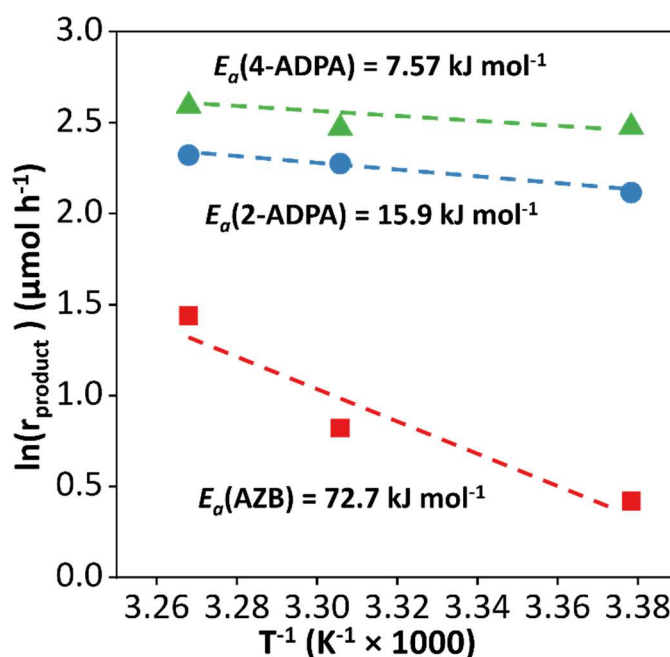
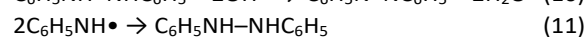
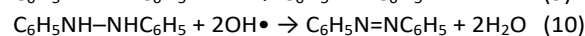
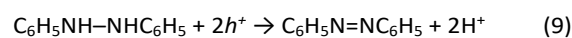


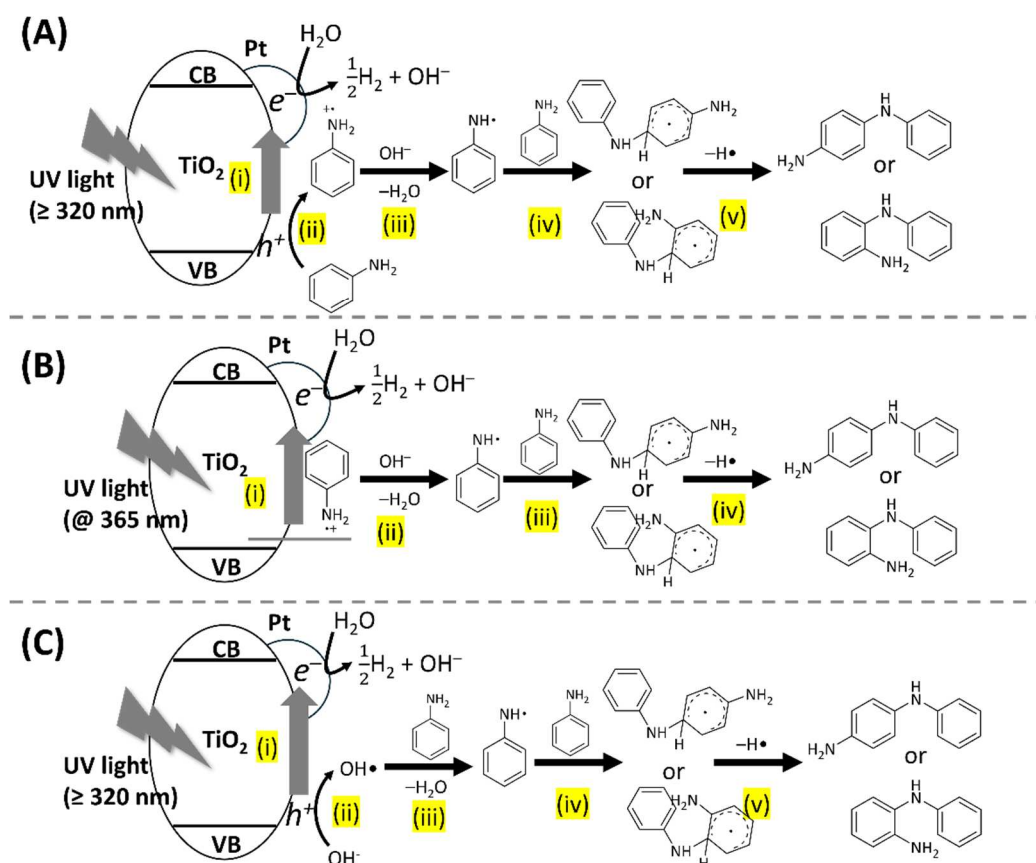
Fig. 3 Pseudo-Arrhenius plots of the products formation rate $\ln(r_{\text{product}})$ for the temperature-controlled reactions. The amount of products recorded at the first 3 min was used for the calculation of the formation rate of products. Reaction conditions: 50 mg of Pt(1.0)/TiO₂ photocatalyst was used; 4.6 μL (50 μmol) of aniline was introduced as the reactant; 4 mL of 0.1 mol L^{−1} of NaOH (aq) was applied as a solvent; The incident UV-LED light wavelength was around 365 ± 5 nm, the irradiated light intensity was 1035 mW cm^{−2} when measured at 360 ± 20 nm in wavelength.

produced from the radical coupling of two anilino radicals, and then oxidized into AZB (eq. 11). If the first photocatalytic N–H bond dissociation in amino group (–NH₂) of aniline to anilino radical species was the RDS for AZB formation, a similar E_a value of AZB as the E_a of 2-ADPA and 4-ADPA would have been observed. The obviously different E_a value indicated that the RDS should be only in the formation process from HyAZB to AZB with a N–H bond dissociation, which could be accelerated by thermal energy.



3.5 Proposed reaction mechanism

In previous reports, it was well-studied that the photocatalytic activation of aniline started from the photogenerated hole (h^+) oxidation into the C₆H₅NH₂^{•+} (aniline radical cation) (eq. 4).^{30,34,35} In this study, in addition to the conventional photocatalytic route, the high selectivity for ADPAs under 365 nm incident light and the corresponding absorption band in the UV-vis spectra, which are attributed to the surface complex formed by aniline and the TiO₂ surface, suggest an alternative mechanism, i.e., the photoexcitation of surface complex with a single electron transfer from nitrogen atom in aniline to titanium atom in TiO₂,



Scheme 1 Proposed one-photon mechanism for ADPAs formation; (A) A general photocatalytic route under UV light (≥ 320 nm), (B) a single electron transfer route from N atom to Ti atom at 365 nm of incident light wavelength and (C) the hydroxyl radical oxidation route. If proton was released from the transition state, a two-photon process would occur.

which resulted in an extra route for C₆H₅NH₂^{•+} radical cation production (eq. 12). Following by a reaction of the C₆H₅NH₂^{•+} radical cation with OH⁻, the anilino radical was formed in alkaline environment (eq. 5). Then the 2-ADPA and 4-ADPA can be produced after the attack of the anilino radical to another aniline molecule by a radical addition-elimination process (eqs. 8 and 13), which is the same process after the conventional photocatalytic route. As another possibility, a radical-radical coupling of anilino radical and 2-aminophenyl radical or 4-aminophenyl radical (•C₆H₄NH₂) cannot be eliminated, which is however quite less possible due to the low concentration of the aminophenyl radical species as the reaction intermediate. Considering the BDE of C₆H₅NH–H (386 kJ mol⁻¹) and that of H–C₆H₄NH₂ (472 kJ mol⁻¹ as H–C₆H₅ in benzene),⁵³ the formation of •C₆H₄NH₂ is relatively difficult so that the possibility of the ADPAs formation via a radical-radical coupling mechanism would be quite low.

Based on those observations in the mechanistic study and so on, the three possible mechanisms for ADPAs production are proposed here: The first is a conventional photocatalytic route (**Scheme 1A**). (i) The UV light photoexcitation of the TiO₂ photocatalyst by the light of 320–400 nm in wavelength generates electrons and holes. The holes move to the TiO₂ surface while the electrons move to Pt nanoparticles (eq. 1). (ii) The aniline molecule is adsorbed by the surface of TiO₂ and

oxidized by the photogenerated holes to give aniline radical cation (eq. 4.); (iii) The formed aniline radical cation is oxidized by OH⁻ to give anilino radical (eq. 5). (iv) Then, anilino radical attacks another aniline molecule in *ortho* or *para* position of the aromatic ring to generate a sp³-type radical transition complex. (v) After the elimination of a H• from this transition state, the 2-ADPA or 4-ADPA molecule as the C–N coupling product was formed (eqs. 8 and 13).

The second route starts from the photoexcitation of the surface complex (**Scheme 1B**). (i) On the TiO₂ surface, the adsorbed aniline molecule is excited by a 365 nm UV light with a single electron transfer from nitrogen atom in aniline to the titanium atom in TiO₂, corresponding the formation of an adsorbed aniline radical cation (eq. 12). (ii–iv) Then the next steps are the same as the (iii), (iv), and (v) in **Scheme 1A**.

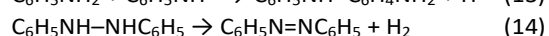
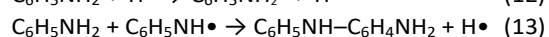
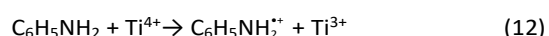
As mentioned in the previous section, a minor route by hydroxyl radicals is also considered here (**Scheme 1C**). (i) The photocatalytic generation of OH• from the reaction of OH⁻ and holes (eq. 6). (ii) The direct oxidation of aniline molecules by OH• to produce anilino radicals and water (eq. 7). (iii–v) Following the attack of an anilino radical to an aniline molecule and the formation of sp³-type radical transition complex, the 2-ADPA or 4-ADPA molecule is then yielded (eqs. 8 and 13).

Considering the relatively small value of *E_a* for both 2-ADPA and 4-ADPA, they are photocatalytically formed without

assistance of thermal catalytic step. The whole C–N bond coupling reaction is a one-photon or two-photon process, and the RDS should be the formation step of the sp^3 -type radical transition state (eq. 8). The small thermal activation energy contributes to thermal step in photocatalytic reaction process proposed in literature.⁵⁷ In the above proposed three mechanisms (**Scheme 1**), the final common step, i.e., the elimination of a H radical in the sp^3 -type radical transition complex to give ADPA was considered to initiate in three possible routes. The first one is the additional oxidation by the photogenerated holes on the TiO_2 surface to the transition complex, which changes the charge distribution of the C–H bond and results in the release of a proton. The second route is the hydrogen abstraction by hydroxyl radicals ($\bullet OH$). The reactive $\bullet OH$ species may react with the H atom to form H_2O . The above two possibilities both required one extra photon, i.e., the direct utilize of holes and the $\bullet OH$ species formation from the oxidation of OH^- by holes, which make the formation of ADPA as a two-photon process. The last one is the catalysis of Pt. It is well-known that Pt nanoparticles can catalyze the broken of C–H bond, such as the catalytic dehydrogenation of propane.⁵⁸ In this study, it is possible that the Pt directly catalyzes the elimination of H atoms in that sp^3 -type radical transition complex.

The formation of AZB has been reported from a successive hole oxidation of HyAZB in the photocatalytic oxidation of aniline. In the present anaerobic conditions, the produced two anilino radicals combine to form a HyAZB molecule (eq. 11), followed by hydrogen abstraction to yield an AZB molecule. This hydrogen abstraction would be promoted by thermal-assisted RDS (eq. 14) or photocatalysis (eqs. 9 or 10).

It is worth noting that hydrogen was also observed as the only detected gaseous product. The process is described in eq. 2. According to the above mechanisms and previous research, the hydrogen gas would predominantly originate from the elimination of hydrogen during the conversion of aniline to form ADPA, AZB, and successive products in the present conditions.



4. Conclusions

In this study, we successfully found a photocatalytic way to synthesize 2-ADPA and 4-ADPA from aniline under a high pH solution. After 30 min reaction, a 19.5% of yield and 77.0% of selectivity were achieved with $Pt(1.0)/TiO_2$ photocatalyst. The limited pH condition ($pH > 11.79$) was found to yield a great amount of ADPA. And the DR UV-vis spectra revealed that a specific absorption peak at 365 nm when aniline was absorbed on the TiO_2 surface, which provided a related high ADPA selectivity in the same wavelength. The kinetic study suggested that neither the dissociation of C–H bond nor the N–H dissociation in aniline is the RDS during the ADPA formation. Then the results of temperature-controlled experiments

revealed that both production of 2-ADPA and 4-ADPA are typical photocatalytic process.

According to the above findings and previous studies, it can be proposed three tentative pathways for the formation of anilino radical. (i) In a typical photocatalytic pathway, the aniline is oxidized by photogenerated holes under UV light irradiation to form aniline radical cation species, then the anilino radical species can be formed by the oxidation of OH^- . (ii) Under an incident photoirradiation of 365 nm wavelength, the adsorbed aniline molecule is photoexcited with a single electron transfer from nitrogen atom in aniline to the titanium atom in TiO_2 , corresponding the formation of an adsorbed aniline radical cation. Then this radical cation can react with OH^- to give anilino radical. (iii) The OH^- reacts with holes to give reactive hydroxyl radical species. After the hydrogen-abstraction by the hydroxyl radical species, the anilino radical species is given. By the above pathways, the formed anilino radical attack another aniline molecule to generate a sp^3 -type radical transition state as the RDS, following by the elimination of hydrogen radical elimination (or, hole oxidation, releasing proton, and reduction of the proton by photoexcited electron), the C–N coupling reaction to give 2-ADPA or 4-ADPA is produced.

The results obtained provide a deeper understanding of photocatalytic C–N coupling, potentially broadening the selectively synthetic strategy for more practical N contained compounds.

Author contributions

Xexin Zou: Investigation, Methodology, Writing – original draft. Akira Yamamoto: Investigation, Funding acquisition. Hisao Yoshida: Conceptualization, Supervision, Writing – review & editing, Funding acquisition.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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